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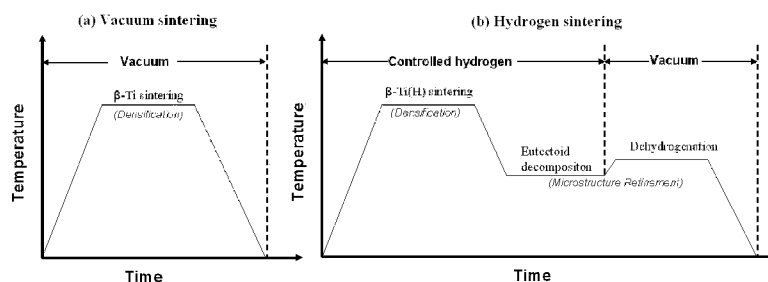
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(54) Title: POWDER METALLURGY METHODS FOR THE PRODUCTION OF FINE AND ULTRAFINE GRAIN TI, AND TI ALLOYS

FIG. 1



(57) Abstract: A process includes sintering TiH_2 and/or Ti metal in a controlled atmosphere, and at elevated temperature, to form a sintered titanium material; cooling the sintered titanium material; and heating the sintered titanium material under vacuum to form titanium metal, or a titanium metal alloy with fine or ultrafine grain sizes; where the controlled atmosphere includes a mixture of hydrogen and an inert gas.

POWDER METALLURGY METHODS FOR THE PRODUCTION OF FINE AND ULTRAFINE GRAIN TI, AND TI ALLOYS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No.: 61/479,177, filed: April 26, 2011, now pending and is hereby incorporated by reference in its entirety.

FIELD

[0002] The technology is generally related to the production of titanium metal and titanium metal alloys.

BACKGROUND

[0003] Powder metallurgy has been regarded as a viable and promising approach for reducing the cost of Ti fabrication because of its near-net-shape capability and potentially melt-less nature of the process. There are generally two kinds of powder metallurgy approaches for making PM titanium products: blended elemental (BE) method and pre-alloyed (PA) method. The BE method in general refers to the pressing and sintering of blended elemental powders. Sintering is generally carried out under vacuum. The PA method refers to sintering pre-alloyed powders, typically produced using gas atomization or plasma rotating electrode techniques. Since pre-alloyed powders have high hardness, and, therefore, poor press-ability if compacted using conventional uni-axial cold pressing methods, pre-alloyed powders are usually consolidated using pressure assisted consolidation techniques such as hot isostatic pressing (HIP). Although PA products in general have better mechanical properties than BE products, the costs of PA products are significantly higher. Therefore, BE is still the preferred cost-effective approach.

[0004] Residual porosity, oxygen contamination, and relatively coarse microstructure after sintering, limits the static and fatigue properties of BE and PM materials. One approach for

reducing residual porosity is to use post-sintering, high pressure processes, such as hot isostatic pressing (HIPing), which can increase the density to greater than 99.8% of the theoretical density. This post-sintering process, however, adds extra cost to BE parts, thereby reducing the cost advantages of the BE method.

[0005] In recent years, an alternative BE technique emerged for titanium production, which is able to produce near pore-free BE parts directly. This technique employs vacuum sintering of titanium hydride (TiH_2) powders instead of Ti metal powder. During sintering, TiH_2 will dehydrogenate at moderate temperatures prior to being sintered at high temperatures under vacuum. Blends of TiH_2 with a 10 wt% 60Al-40V master alloy powder can be sintered to 98.5%–99.5% of the theoretical density in as-sintered state, in contrast to 90%–95% of the theoretical density when titanium powder was used. Although PM Ti parts produced by sintering using TiH_2 powder have shown great potential, the grain size of as-sintered materials are usually large. The as-sintered microstructure for Ti-6Al-4V consists of coarse Widmanstätten lamellar alpha plate colony structures which have a coarse microstructure that is not optimum with respect to tensile or fatigue strength. The as-sintered coarse microstructures can be refined only by post-sintering thermal mechanical working and heat treatments, which, once again, increase the cost of PM Ti parts, reducing the economic benefits of PM Ti.

SUMMARY

[0006] In one aspect, a microstructure engineering approach is provided to produce PM titanium alloys with a fine grain microstructure, and other desired microstructure features. Such features lead to improved mechanical properties, without having to rely on subsequent processing steps, such as thermal mechanical working, after sintering

[0007] A process is provided that includes sintering TiH_2 or Ti metal powders in a controlled atmosphere, and at elevated temperature, to form a sintered titanium material containing hydrogen; cooling the sintered titanium material; holding the sintered titanium material at a hold temperature and a hold time sufficient for eutectoid decomposition of the sintered titanium material; and heating the sintered titanium material under vacuum at a temperature which is less than that of the sintering temperature; where the controlled atmosphere

includes a mixture of hydrogen and an inert gas. In one embodiment, the sintering also includes sintering the TiH_2 in the presence of an alloying additive. In any of the above embodiments, the inert gas includes helium, argon, or xenon.

[0008] In any of the above embodiments, the sintered titanium material may include titanium solid solutions phases: α , δ and β phases. In any of the above embodiments, the titanium metal or the titanium metal alloy obtained from the process may have a grain size of less than 10 μm . In some such embodiments, the titanium metal or the titanium metal alloy obtained from the process has a grain size of from about 10 nm to about 10 μm . In some such embodiments, the titanium metal or the titanium metal alloy obtained from the process has a grain size of from about 10 μm to about 100 μm . In any of the above embodiments, the titanium metal or the titanium metal alloy may have a density greater than 95%. In some such embodiments, the titanium metal or the titanium metal alloy has a density of greater than 98%. In any of the above embodiments, the titanium metal or the titanium metal alloy may have an oxygen content of less than 0.5 wt%. In some such embodiments, the titanium metal or the titanium metal alloy has an oxygen content of from about 0.001 wt% to about 0.3 wt%. In any of the above embodiments, the TiH_2 or Ti metal may be provided as a powder. In some such embodiments, the powder has an initial size from about 20 mesh to about 600 mesh.

[0009] In any of the above embodiments, the elevated temperature is from about 1000°C to about 1500°C. In any of the above embodiments, the sintering is conducted from about 1 hour to about 240 hours. In any of the above embodiments, the re-heating for eutectic decomposition is conducted from about 200°C to about 900°C, below β -phase transition temperature which is a function of alloy compositions. In any of the above embodiments, the re-heating for eutectic decomposition is conducted from about 1 hour to about 24 hours. In any of the above embodiments, the hydrogen to inert gas ratio in the controlled atmosphere is from 1:100 to 1:1. In any of the above embodiments, the hold temperature for dehydrogenation in vacuum is from about 300°C to about 800 °C below the β -phase transition temperature. In any of the above embodiments, the hold time is conducted from about 2 hours to about 100 hours depending on the size of the components.

[0010] In any of the above embodiments, the process may be void of mechanical processing steps after sintering. As used herein, the term “mechanical processing steps” refers to forging, rolling, extrusion, drawing, swaging, and the like as known in the art. In any of the above embodiments, the process may also include powder milling of the TiH_2 or Ti and the alloying additive, if present. In any of the above embodiments, the process also includes blending of the TiH_2 and/or Ti and the alloying additive, if present.

[0011] In another aspect, a material is provided that includes any of the titanium metal or titanium metal alloys produced by any of the above processes. The material may be a commercially pure titanium (CP-Ti). CP-Ti is a term that is widely used in the art. CP-Ti is classified on scale of Grade 1 to 5, each level of the scale being based upon the oxygen content and/or alloying according to industry standards. Alternatively the material may be a commercial alloy of Ti. In one embodiment, the material is Ti-6Al-4V.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a graphical representation of an illustrative temperature vs. time cycle for titanium production, according to one embodiment.

[0013] FIG. 2 is an SEM micrograph illustrating the ultrafine microstructure of a Ti-6Al-4V alloy produced according to the examples.

[0014] FIG. 3 illustrates a shrinkage curve of controlled hydrogen sintering of TiH_2 -AlV, according to the examples.

[0015] FIG. 4 is a group of SEM and TEM micrographs showing the microstructures produced by vacuum sintering of TiH_2 (FIG. 4A: SEM image), hydrogen sintering of TiH_2 (FIG. 4B: SEM image; FIG. 4C: TEM image), typical wrought processes (FIG. 4D: SEM image) and vacuum sintering of Ti metal powder (FIG. 4E: SEM image), according to the examples.

DETAILED DESCRIPTION

[0016] A process is provided for producing Ti and Ti alloys with near-full density, and fine or ultrafine grain sizes in an as-sintered state without, or with only minimal, post-sintering

processing. The ultrafine grain and near-porosity-free microstructure of the resulting material allows for flexibility in custom engineering of the microstructure of Ti materials. The near porosity-free ultrafine microstructure is achieved by sintering under atmospheres with a controlled partial pressure of H_2 at high temperatures, followed by subjecting the material to eutectoid transformation and dehydrogenation at moderate temperatures. The thermal cycle is designed such that the phase transformations during the eutectoid reaction and dehydrogenation are controlled so that they lead to ultrafine microstructure features without significant grain growth. The process provides for powder compacts of titanium with alloying elements (*e.g.* Ti-6Al-4V) that can be sintered to full density ($>99\%$ rel. density) under a partial H_2 atmosphere, and that exhibit grain sizes, after dehydrogenation, which can be refined to less than 1 micrometer (μm). In one embodiment, H_2 is controlled during sintering. In comparison to vacuum sintering of Ti-6Al-4V powder, the present process controls the partial pressure of H_2 in the atmosphere, and hydrogen content in the powder throughout the sintering process.

[0017] The process includes three primary steps: (1) β -Ti(H) densification, (2) eutectoid decomposition, and (3) dehydrogenation in vacuum. FIG. 1 illustrates the process in a graph of temperature v. time. FIG. 1 illustrates that ramping up and down of the temperature in each of the steps and the hold periods that may be used. Note that the steps may be completely separated as separate processes conducted in different runs, or as a single integrated continuous run. Without being bound by theory, the following steps describe what are believed to be the phase transitions that occur to prepare the titanium and titanium alloys having fine grain size.

[0018] In the first step of β -Ti(H) densification, by controlling the H_2 atmosphere, the process maintains sintering in β -Ti phase region. Self-diffusion of the titanium in the β -Ti phase is significantly faster than in the α -Ti phase, and a solid solution of hydrogen atoms in titanium can reduce the activation energy of Ti self-diffusion due to the decrease of Ti-Ti bonding strength. It is believed that each of these effects help to achieve full densification during β -Ti(H) sintering.

[0019] In the second step of eutectoid decomposition, the densified samples are cooled in a controlled H_2 atmosphere to temperatures below the eutectoid reaction, and holding the samples at this temperature for a period of time to complete the eutectoid reaction. As used

herein, the term “eutectoid reaction” refers to the formation of new phases (α -Ti(H) + δ -TiH_x) that precipitate in the interior of the β -Ti(H) grains. As a result, the coarse β -Ti(H) grains break into finely dispersed (α -Ti(H) + β -Ti(H)+ δ -TiH_x) grains, thereby refining the microstructure.

[0020] In the third step of dehydrogenation in vacuum, the hydrogen atoms in the titanium are removed by vacuum annealing. The phase transformations during dehydrogenation further refine and modify the microstructure. The hydrogen can be removed to a level much lower than allowable levels according to ASTM standards (150 ppm). For example, the residual hydrogen content after vacuum sintering of TiH₂ or thermohydrogen processing (THP) can be as low as 10 ppm, which is not detrimental to the mechanical properties of titanium materials.

[0021] A process of powder metallurgy technology includes producing titanium metal and titanium metal alloys. The process may be used to produce low-cost Ti alloys that are nearly fully dense (>99%CP-Ti, >98%Ti-6Al-4V) Ti materials and which have a fine, and/or ultrafine, grain size. The processes also provide for sintering titanium metal in hydrogen to produce near full dense titanium materials. Such ultrafine grain sizes on the microscopic scale provide for high strength and ductility in the macroscale materials. The process employs a microstructure engineering approach of controlling densification and phase transformation processes during sintering of titanium hydride (TiH₂) and/or Ti metal and alloying powders to form a sintered titanium material.

[0022] In one aspect, the process includes sintering blended powder of TiH₂ and/or Ti metal and alloying powders in a controlled atmosphere with a partial pressure of hydrogen (H₂) gas, to form a sintered titanium material containing hydrogen. The controlled atmosphere may also contain an inert gas such as helium, argon, or xenon. Using Ti-6Al-4V as an example, under the partial hydrogen pressure, blended powder sinters to near full density with a microstructure having one, two, or three phases including alpha (α), delta (δ) and beta (β) phases after cooling to room temperature. After cooling, the sintered titanium material is then re-heated under vacuum to dehydrogenate. The material is then re-cooled to form a titanium metal alloy with a microstructure having alpha (α) and beta (β) phases. The sintering in the controlled atmosphere, eutectoid decomposition, and the dehydrogenation under vacuum, can be three separate processes, or they can be integrated in a single process. Alternatively, the first and

second step may be processed in sequence with the third step following later, or the first step may be completed with the second and third steps being processed together later. The single, integrated process of all three steps includes sintering blended powders of TiH_2 and alloying powders in a controlled atmosphere with a partial pressure of hydrogen (H_2) gas, cooling and holding for eutectoid decomposition, and then switching the atmosphere condition to vacuum, or very low pressure, conditions at certain temperatures during the cooling step of the sintering process.

[0023] As used herein, the term “near full density” refers to a minimization of porosity in the material, such that if full density were achieved, the density of the bulk material would be equal to that of the theoretical density of the material. As used herein, near full density refers to the material having a relative density of greater than 98%. As used herein, and as eluded to above, full density refers to the material having a relative density of greater than 99%.

According to some embodiments, the titanium metal or the titanium metal alloy has a relative density greater than 97%. In other embodiments, the titanium metal or the titanium metal alloy has a near full density. In other embodiments, the titanium metal or the titanium metal alloy has a full density.

[0024] As used herein, the term α -phase refers to a hexagonal close-packed (HCP) solid solution of Ti with alloying elements. The α -phase may or may not contain some hydrogen. The term δ -phase refers to a face-centered cubic (FCC) titanium hydride, TiH_x , where x varies from 1.5 to 2, at room temperature. The term β -phase refers to a body-centered cubic (BCC) Ti solid solution with alloying elements, which may or may not also contain hydrogen. The definitions of the phases are further illustrated by the phase diagrams of Ti-H, and Ti-6Al-4V-H (ASM Handbook, Vol 3, p238, 1992). It should be noted that the phase diagrams of a titanium alloy with hydrogen vary considerably with the exact composition of the alloy. Therefore, the exact temperatures and time of sintering, isothermal holding for eutectoid transformation, and dehydrogenation will all vary accordingly.

[0025] In the first step of β -Ti(H) densification, the sintering is conducted at a temperature from about 1100°C to about 1500°C to form a β -Ti(H) densified material. The

sintering is also conducted for a time period sufficient to gain near full density. According to various embodiments, the sintering time may vary from about 30 minutes to about 30 hours. According to some embodiments, the sintering is performed from about 1 hour to 24 hours. The sintering may be conducted in any chamber in which the temperature and atmosphere may be controlled. For example, the sintering may be conducted in a furnace which is capable of attaining a working temperature of up to 1500°C or even higher, is capable of being used under vacuum, and is capable of using gases such as hydrogen, argon, nitrogen, and the like, or a mixture of any two or more such gases. The heating elements of the furnace may be made of those as are known in the art, including, but not limited to, tungsten or molybdenum mesh, silicon carbide, or MoSi₂.

[0026] In the second step of eutectoid decomposition, the β -Ti(H) densified material is held at a temperature sufficient for the above-described decomposition to take place and form a eutectoid decomposed material. For example, the temperature may range from about 200°C to about 800°C depending on exact alloy compositions. In some embodiments, the temperature ranges from about 500°C to about 700°C for Ti-6Al-4V alloy and 150°C to about 300°C for CP-Ti. The time period for eutectoid decomposition is sufficient for the process to proceed sufficiently toward completion. For example, the temperature may be held constant, or nearly constant, from about 10 minutes to about 12 hours. In some embodiments, the temperature may be held constant, or nearly constant, from about 30 minutes to about 6 hours.

[0027] After formation of the eutectoid decomposed material, the material is re-heated to a temperature from about 500°C to about 900°C under a vacuum. At this temperature, the sintered material releases the hydrogen by a process called dehydrogenation, and the material may then form the fine grain microstructure. According to various embodiments, if the material is a Ti-6Al-4V alloy, such fine grain microstructure includes both α -phases and β -phases. The re-heating of the material may be conducted for a time period sufficient to reduce hydrogen content in materials to less than 150 ppm. Without being bound by theory, the reheating-dehydrogenation process is believed to decompose the δ - phase and release the hydrogen in the material. During the reheating process, the δ - phase transforms to a α + β phase mixture. Hydrogen then diffuses through the material to the surface, where it escapes as hydrogen gas.

The time of the reheating process may vary depending on the size of the specimen, or the components used. The reheating process may be conducted for from 1 hour to about 100 hours, at the temperature. The actual time required is governed by the law of diffusion. According to some embodiments, the re-heating is performed from about 10 to 24 hours. The dehydrogenation may be conducted in the same chamber as the initial sintering, or in a separate furnace chamber in which the temperature and atmospheric pressure may be controlled.

[0028] According to various embodiments, the TiH_2 is provided as a powder for the sintering step. The powder may have a size from about 20 mesh to about 600 mesh. In one embodiment, the powder has a size of from about 100 mesh to about 400 mesh. In one embodiment, the powder has a size of about -200 to +325 mesh. In another embodiment, the powder has a size of about 40 mesh. Usually, the coarser the initial powder, the lower the final oxygen content of the material. When using traditional powder metallurgy methods to make titanium components from titanium metal powders, coarse powders are very difficult to consolidate, and also lead to coarse final microstructure. In contrast, fine Ti metal powders are prone to oxygen contamination. The present technology allows for use of a coarse TiH_2 powder as the starting raw material, thereby making it easier to control oxygen content in the subsequent powder pressing, forming, sintering, and dehydrogenation steps, while coarse TiH_2 powder poses few difficulties in densification to near full density provided that proper powder processing and compaction techniques are used.

[0029] In the present methods and materials, the use of coarse powders does not lead to coarse final grain microstructure because of the controlled stages of densification and phase transformation. The grain sizes of the final material do not depend as much on the initial particle size of the powder as does the titanium metal powder, but rather the grain size is primarily a function of the kinetics and temperature versus time profiles of both the densification and the dehydrogenation steps.

[0030] The materials prepared by the above processes are achieved at lower cost because of the high yield of the processes, fewer processing steps, and lower energy consumption, compared to materials produced by traditional wrought alloy methods. The traditional wrought alloy methods refers to the manufacturing process by melting, casting, hot working, cold

working and machining. The materials prepared by the presently described processes have fine grain sizes, and thus exhibit equivalent or superior mechanical properties to traditionally wrought alloys. Finally, the instant materials have lower oxygen content than equivalent titanium materials prepared using traditional powder metallurgy approaches, and are substantially free of impurities. For example, in some embodiments, the titanium metal or titanium metal alloy prepared using the above process has a grain size of less than 100 μm . In some embodiments, the titanium metal or titanium metal alloy prepared using the above process has a grain size of less than 5 μm . In other embodiments, the titanium metal or the titanium metal alloy has a grain size of from about 10 nm to about 10 μm . In other embodiments, the titanium metal or the titanium metal alloy has a grain size of from about 10 μm to about 100 μm .

[0031] In other embodiments, the titanium metal or titanium metal alloy has an oxygen content of less than 0.5 wt%. In other embodiments, the titanium metal or titanium metal alloy has an oxygen content of less than 0.2 wt%. In other embodiments, the titanium metal or titanium metal alloy has an oxygen content of from about 0.001 wt% to about 0.3 wt%.

[0032] It is noted that the above processes are void of post-sintering mechanical processing steps as a part of material manufacturing process. As used herein, mechanical process steps are those steps where the material is deliberately deformed plastically at either elevated (thermal mechanical or hot working) or room temperatures (cold working). After the plastic deformation of cold working, or during hot working the microstructure of the material is transformed at elevated temperatures *via* recrystallization to achieve desired microstructure. The desired fine grain microstructure is formed *in situ* during the integrated densification-dehydrogenation process. In some cases, thermal mechanical working may be done to further enhance the properties.

[0033] In another aspect, a titanium metal or titanium metal alloy produced by any of the above processes is provided. For example, the titanium metal or titanium metal alloy may have a relative density of 98 % or greater. In some embodiments, the titanium metal or titanium metal alloy has a relative density of 99 % or greater. In some embodiments, the titanium metal or titanium metal alloy has a relative density of from about 99 % to about 99.9%. The titanium

metal or titanium metal alloy produced by any of the above processes may have a grain size of less than 100 μm . In some embodiments, the titanium metal or titanium metal alloy produced by any of the above processes has a grain size of less than 5 μm . In other embodiments, the titanium metal or the titanium metal alloy produced by any of the above processes has a grain size of from about 10 nm to about 10 μm . In other embodiments, the titanium metal or the titanium metal alloy produced by any of the above processes has a grain size of from about 10 μm to about 100 μm . The titanium metal or titanium metal alloy produced by the any of the above processes may have an oxygen content of less than 0.5 wt%. In other embodiments, the titanium metal or titanium metal alloy has an oxygen content of less than 0.2 wt%. In other embodiments, the titanium metal or titanium metal alloy has an oxygen content of from about 0.001 wt% to about 0.3 wt%.

[0034] The titanium metal or titanium metal alloy materials above may find utility in any of a number of applications where titanium and its alloys are currently used, or will be used. For example, the materials may be used in, but not limited to, automobile parts, biomedical implants, medical surgical tools, aircraft equipment, diving equipment, oil field equipment, sports equipment, chemical equipment, food processing equipment, among others.

[0035] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0036] The present technology, thus generally described, will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting.

EXAMPLES

[0037] **Example 1.** Commercial TiH_2 powder (46.8750 g) and 60Al-40V alloy powder (5.0000 g) were blended using a tumbler mixer. The particle size of both the TiH_2 and the 60Al-

40V alloy powders were -325 mesh. The blended powders were cold isostatically pressed at 350 MPa (megapascal) to prepare a cylindrical sample about 15 mm in diameter and about 70 mm in length. The sample was then heated in an alumina tube furnace (76 mm in diameter by 1200 mm long) up to 1200°C at 10°C/min. The sample was held at that temperature for 4 hours under a specific atmosphere. The samples were then cooled to 650°C at a rate of 5°C per minute and held at this temperature for 4 hours. The sample was then cooled to room temperature in the furnace. A molybdenum crucible was used as the sample holder during sintering process. The entire sintering process was conducted in a stream of high purity argon (purity > 99.999%, O₂% < 1 ppm, H₂O < 1 ppm) and hydrogen (purity > 99.999%, O₂% < 1 ppm, H₂O < 2 ppm) with a slightly positive pressure. The flow rates of the argon and hydrogen were 1.8 L/min and 320 mL/min, respectively. The sample was then re-heated in the alumina tube under vacuum condition (10⁻⁴ Pa) to 700 °C at a heating rate of 10°C /min and held at this temperature for 8 hours for dehydrogenation. A schematic of the heating profile is illustrated in FIG. 1. FIG. 2 is a photograph of the fine grain material produced. In FIG. 2, the mean grain size of the β phases is about 0.5 μm (bright spots), and the mean grain size of α phases is about 1-4 μm (dark color) in as-dehydrogenated article. The relative density of the material was 98.5%.

[0038] **Example 2.** Production of Ti-6Al-4V alloy. Ti metal, TiH₂, and Al-V master alloy powders were supplied by Reading Alloys. The powders were mixed according to compositions of Ti-6Al-4V alloy. Cylindrical powder compacts were made in a cold iso-static press (CIP) using 350 MPa pressure. Dimensions of the green compacts were approximately φ15 x L60 mm. The compacts were then subjected to sintering in either vacuum or partial hydrogen atmosphere. In the case of vacuum sintering, vacuum level was 10⁻⁵ torr. In the case of atmospheric sintering, mixtures of H₂ with Ar were used. The atmosphere is slightly positive, meaning slightly higher than 1 atm.

[0039] *Near full densification.* Density measurements show specimens produced by both vacuum and atmospheric sintering have near full densification (~99% relative densities) after sintering, and the near full densification is also verified by the SEM images that show very few pores. FIG. 3 shows the densification of the specimen after sintering in hydrogen prior to dehydrogenation. The volume expansion near the end of the curve is due to the increase of

hydrogen content at lower temperatures. It demonstrates that β -phase titanium can be densified with significant hydrogen content in the material in a partial hydrogen atmosphere. This is a significant finding that makes the entire processing scheme possible to achieve full densification with fine microstructure.

[0040] *Microstructure refinement.* FIG. 4 shows SEM (scanning electron microscope) micrographs of the as-sintered microstructures of both vacuum sintered (FIG. 4A) and those sintered in partial hydrogen (FIG. 4B). The SEM micrographs show that the microstructures produced by these two processes are drastically different. The specimen produced by vacuum sintering show typical coarse ($\alpha + \beta$) lamellar microstructure (FIG. 4A: α in dark and β in bright contrast; β phase distributed at inter-granular α phases), which is the typical as-sintered microstructure of Ti-6Al-4V alloy by BE processes using Ti metal powder. In contrast, the specimen of sintered in hydrogen shows a clearly different microstructure. The microstructure produced by the hydrogen sintering process consists of ultrafine broken-up β phases (bright) in the matrix of refined α phases (dark contrast) as shown in FIG. 4B. The refined microstructure is further examined using a transmission electron microscope (TEM; FIG. 4C). Based on the SEM and TEM images, the mean grain size of β phases is about 0.5 μm and the mean grain size of α phase is about 1 μm . As used herein, the term “hydrogen sintering” refers to sintering in pure hydrogen gas or in a gas mixture that contains hydrogen.

[0041] FIG. 4 also compares the microstructure of hydrogen sintered Ti to typically annealed, wrought Ti-6Al-4V (FIG. 4D), and typical vacuum sintered Ti metallic powder (FIG. 4E). The vacuum sintered TiH_2 powder is almost identical to that of vacuum sintered Ti metallic powder as it should be, albeit that the density of sintered TiH_2 is usually higher than that of sintered Ti under similar conditions. Compared to the wrought microstructure as shown in FIG. 4D, the hydrogen-sintered Ti microstructure is finer. It should be noted that the microstructure of wrought materials can vary significantly depending on exact thermomechanical processing history.

[0042] The microstructure produced by the above methods have many advantages over coarse lamellar structure of conventional sintered Ti materials, particularly with respect to mechanical properties. In comparison to wrought Ti materials, the microstructure of materials

produced and described above, show that such refined microstructure leads to improved tensile and fatigue properties as compared to the coarse lamellar microstructure. Evaluations of basic tensile mechanical properties were carried out and are present in Table 1. Table 1 compares the tensile mechanical properties of the as-sintered, microstructured specimens produced herein (hydrogen-sintered) with ASTM standards as well as vacuum sintered Ti-6Al-4V.

Table I: Impurity Concentrations And Tensile Properties Of Vacuum-Sintered And Hydrogen-Sintered Ti-6Al-4V

	Tensile strength (MPa)	0.2% Yield strength (MPa)	Elongation (%)	O (wt%)	H (wt%)	C (wt%)	N (wt%)
ASTM B348	895	828	10	0.20	0.015	0.08	0.05
Vacuum-sintered	982	859	12	0.302 ±0.044	0.004 ±0.002	0.080 ±0.012	0.025 ±0.007
Hydrogen-sintered	1036	943	15	0.308±0.07	<0.003	----	----

[0043] From Table 1 it is observed that the tensile strength and ductility of the hydrogen-sintered material is slightly higher than that of the vacuum-sintered material. Without being bound by theory, it is believed that this difference is attributable to the finer grain size.

[0044] Table 1 also shows the chemical analysis of the as-sintered specimen. It illustrates that the oxygen content of these specimens is higher than that of ASTM standard for wrought material. The oxygen content can be further reduced by controlling powder material handling procedures. The hydrogen content in the finished specimen is sufficiently low to meet ASTM standards. Carbon and nitrogen content of the material also meet the ASTM standards.

[0045] The above-described processes are designed to take advantage of both the higher sintered density under hydrogen and the phase transformation induced by hydrogen that produces fine grain sizes. The sintering is conducted in β -Ti(H) solid solution phase region rather than pure metallic state in vacuum. The results presented above demonstrate that titanium can indeed be sintered to very high density at high temperatures, *e.g.* in the β -phase region, under controlled

hydrogen partial pressure with significant hydrogen content in the metal. At the sintering temperature, the material is a solid solution of β -phase titanium with hydrogen.

[0046] It is important to note that being able to sinter titanium in a controlled atmosphere is a significant discovery. Conventionally, Ti must be sintered in vacuum in order to achieve high density and low oxygen. Sintering of Ti under argon atmosphere produces a product with unacceptable residual porosity and oxygen levels. In addition to the benefits with respect to microstructure and mechanical properties, being able to sinter titanium in a partial hydrogen atmosphere also opens a door to continuous production of PM Ti parts which has significant cost advantages over batch processes such as vacuum sintering.

[0047] The results presented above demonstrate that Ti and Ti alloy powders can be sintered to near full density in partial hydrogen atmosphere at temperatures when β -Ti forms solid solution alloys with hydrogen. By controlling the eutectic phase transformation from β to $\alpha+\delta$ and the subsequent dehydrogenation process, near-fully dense Ti material with very fine microstructure can be obtained in as-sintered state without resorting to thermomechanical working. This is a promising approach for producing PM Ti materials with superior mechanical properties at minimum cost.

[0048] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (*i.e.*, meaning “including, but not limited to,”) unless otherwise noted. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Additionally the phrase “consisting essentially of” will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed invention. The phrase “consisting of” excludes any element not specifically specified.

[0049] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0050] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0051] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0052] While various aspects and embodiments have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A process comprising:
 - sintering TiH_2 and/or Ti metal in a controlled atmosphere, and at elevated temperature, to form a sintered titanium material containing hydrogen;
 - cooling the sintered titanium material;
 - holding the sintered titanium material at a hold temperature and a hold time sufficient for eutectoid decomposition of the sintered titanium material;
 - and
 - heating the sintered titanium material under vacuum at a temperature which is less than that of the sintering temperature;wherein:
 - the controlled atmosphere comprises a mixture of hydrogen and an inert gas.
2. The process of Claim 1, wherein the sintering further comprising sintering the TiH_2 and/or Ti metal in the presence of an alloying additive.
3. The process of Claim 1 or 2, wherein the inert gas comprises helium, argon, or xenon.
4. The process of any one of Claims 1-3, wherein the sintered titanium material comprises a microstructure comprising α -phases, δ -phases and β phases.
5. The process of any one of Claims 1-4, wherein the elevated temperature is from about 1000°C to about 1500°C.
6. The process of any one of Claims 1-5, wherein the sintering is conducted from about 1 hour to about 30 hours.
7. The process of any one of Claims 1-6, wherein the hold temperature is from about 500°C to about 800°C.
8. The process of any one of Claims 1-6, wherein the hold temperature is from about 150°C to about 300°C.

9. The process of any one of Claims 1-8, wherein the hold time is conducted from about 10 minutes to about 120 hours.
10. The process of any one of Claims 1-9, wherein the re-heating is conducted from about 400°C to about 900°C.
11. The process of any one of Claims 1-10, wherein the re-heating is conducted from about 1 hour to about 20 hours.
12. The process of any one of Claims 1-11, wherein the titanium metal or the titanium metal alloy obtained from the process has a grain size of less than 10 μm .
13. The process of Claim 12, wherein the titanium metal or the titanium metal alloy obtained from the process has a grain size of from about 10 nm to about 10 μm .
14. The process of Claim 12, wherein the titanium metal or the titanium metal alloy obtained from the process has a grain size of from about 10 μm to about 100 μm .
15. The process of any one of Claims 1-14, wherein the hydrogen to inert gas ratio in the controlled atmosphere is from 1:100 to 1:1.
16. The process of any one of Claims 1-15, wherein the titanium metal or the titanium metal alloy has a density greater than 96%.
17. The process of any one of Claims 1-15, wherein the titanium metal or the titanium metal alloy has a density of greater than 98%.
18. The process of any one of Claims 1-15, wherein the titanium metal or the titanium metal alloy has a density of greater than 99%.
19. The process of any one of Claims 1-15, wherein the titanium metal or the titanium metal alloy has a density from about 98% to about 99%.
20. The process of any one of Claims 1-19, wherein the titanium metal or the titanium metal alloy has an oxygen content of less than 0.5 wt%.

21. The process of any one of Claims 1-19, wherein the titanium metal or the titanium metal alloy has an oxygen content of from about 0.001 wt% to about 0.3 wt%.
22. The process of any one of Claims 1-21, wherein the TiH_2 is provided as a powder.
23. The process of any one of Claims 1-21, wherein the Ti metal is provided as a powder.
24. The process of Claim 23, wherein the powder has an initial size from about 20 mesh to about 600 mesh.
25. The process of Claim 23, wherein the powder has a size of from 100 to 325 mesh.
26. The process of any one of Claim 1-25, which is void of post-sintering mechanical processing steps.
27. The process of any one of Claim 1-26 further comprising powder milling of the TiH_2 and the alloying additive, if present.
28. The process of any one of Claim 1-26 further comprising blending of the TiH_2 and the alloying additive, if present.
29. A material comprising titanium metal or titanium metal alloy produced by the process of any one of Claims 1-28.
30. The material of Claim 29 which is commercially pure titanium.
31. The material of Claim 29 which is Ti-6Al-4V.

FIG. 1

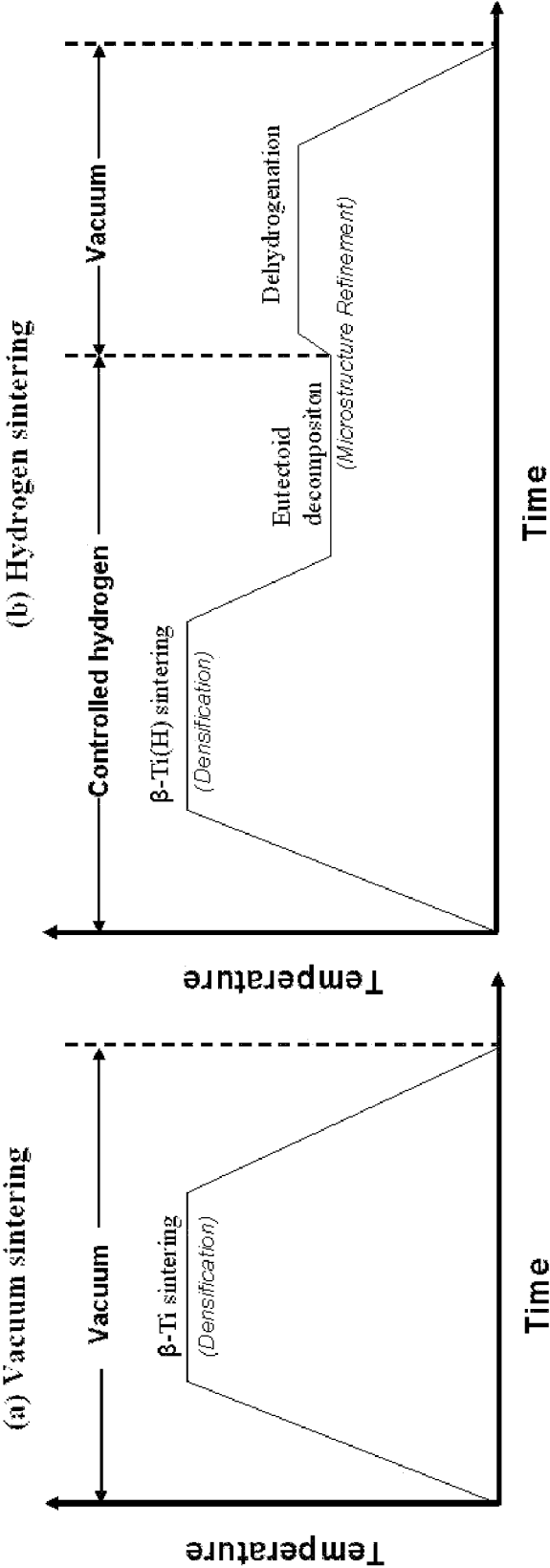


FIG. 2

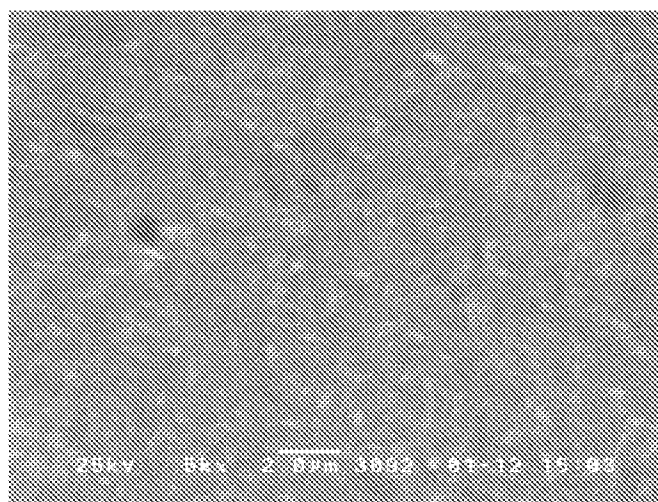


FIG. 3

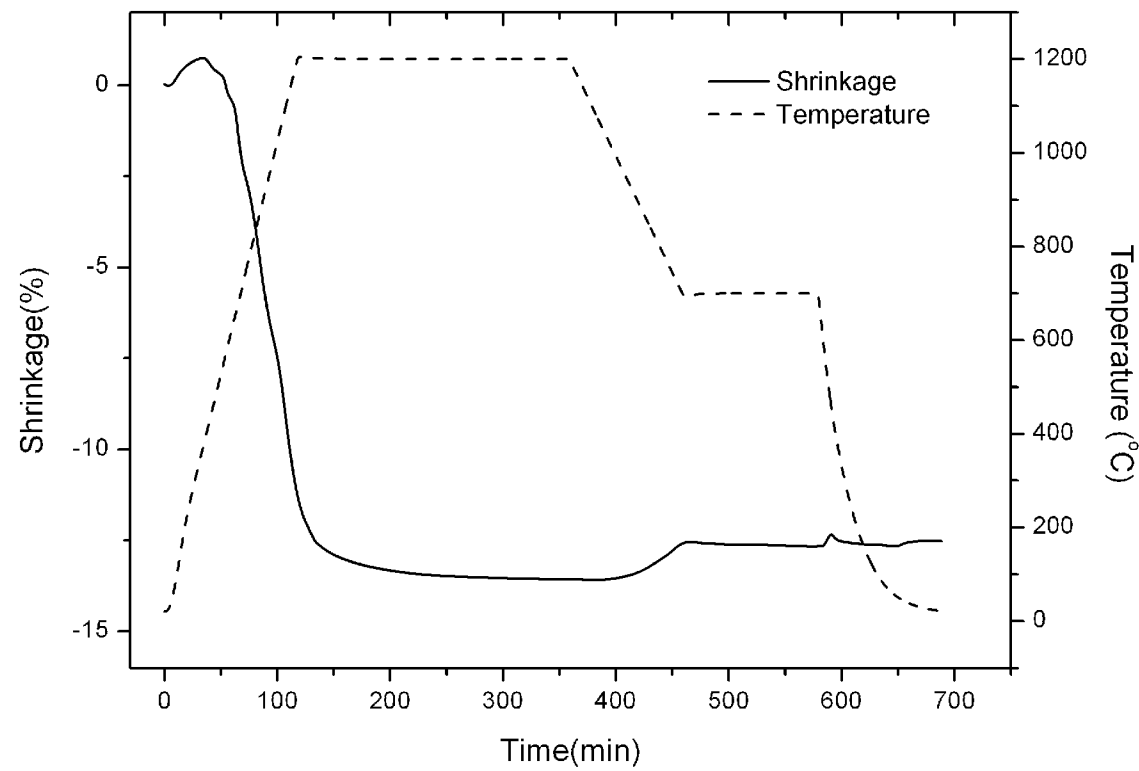
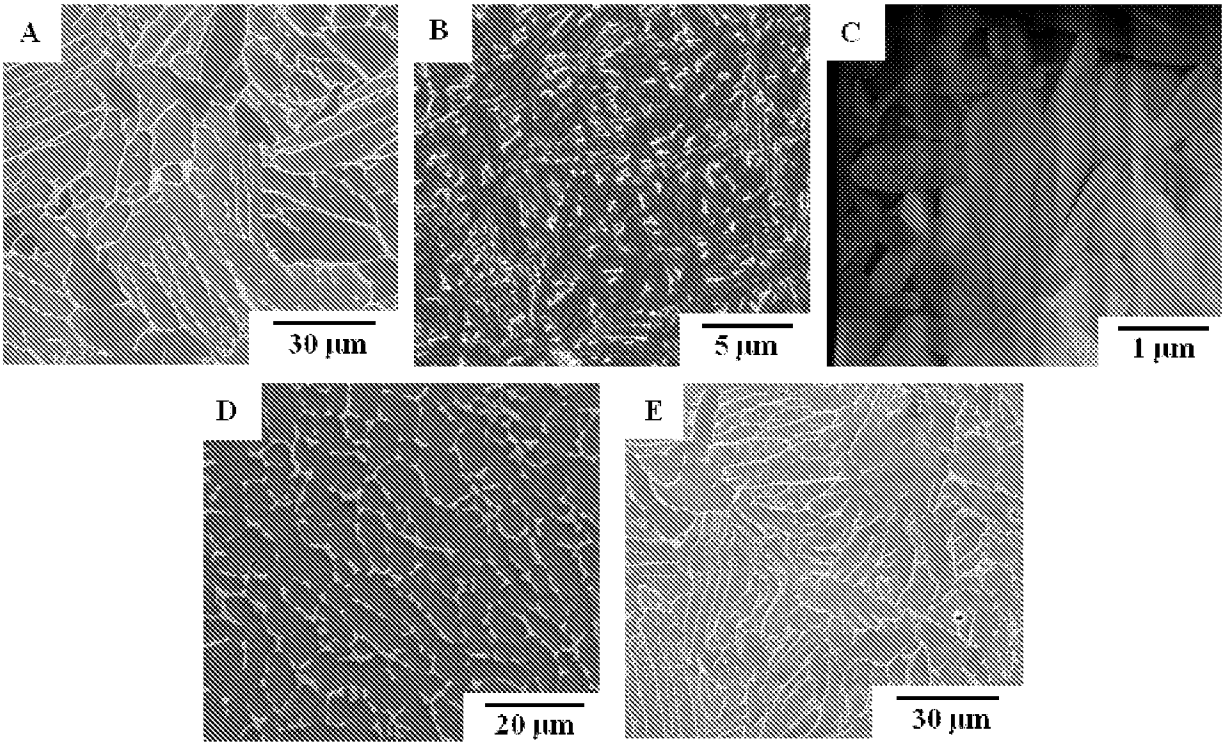


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/061685**A. CLASSIFICATION OF SUBJECT MATTER***C22C 1/04(2006.01)i, C22C 14/00(2006.01)i, B22F 1/00(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 1/04; C22C 14/00; C22F 1/00; C22C 1/65; C22C 1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: titanium metal, sintering, hydrogen, eutectoid decomposition, grain size

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 4923513 A (PAUL DUCHEYNE et al.) 08 May 1990 See the abstract; columns 7,13; and claims 1,5,10,14,16,18,21-23.	1-7,9-13,29,31 8,14-28,30
A	US 5447582 A (DANIEL EYLON et al.) 05 September 1995 See the abstract; column 3; and claims 1,4,6.	1-31
A	US 5108517 A (KINICHI KIMURA et al.) 28 April 1992 See the abstract; column 8; and claims 1,2.	1-31
A	US 5024813 A (KATSUHIRO NISHIYAMA) 18 June 1991 See the abstract; column 6; and claims 1,3.	1-31

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 JUNE 2012 (26.06.2012)

Date of mailing of the international search report

02 JULY 2012 (02.07.2012)

Name and mailing address of the ISA/KR

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Facsimile No. 82-42-472-7140

Authorized officer

JUNG Sug Woo

Telephone No. 82-42-481-8443



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2011/061685

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4923513 A	08.05.1990	None	
US 5447582 A	05.09.1995	None	
US 5108517 A	28.04.1992	CN 1023495 C	12.01.1994
		CN 1050413 A	03.04.1991
		CN 1050413 C0	07.11.1993
		EP 0411537 A1	06.02.1991
		EP 0411537 B1	24.04.1996
		JP 03-130351 A	04.06.1991
		JP 03-197655 A	29.08.1991
		JP 03-277752 A	09.12.1991
US 5024813 A	18.06.1991	JP 02-129329 A	17.05.1990
		JP 06-017524 B2	09.03.1994
		JP 1892575 C	26.12.1994

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2011/061685**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- I. Claims 1-28 are directed to a process.
- II. Claims 29-31 are directed to a material comprising titanium metal alloy produced by the process of any one of claims 1-28.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.